KnE Materials Science

TECHNOGEN-2019
IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"
Volume 2020

Knowledge E
enriching | engaging | empowering

Conference Paper

Electroflotation Extraction of Sparingly Soluble Compounds of Titanium (TiO_2) from Liquid Technogenic Waste

V.A. Kolesnikov, A.V. Perfileva, V.S. Kasyanov, S.A. Kabanova, and A.V. Kolesnikov

D. Mendeleev University of Chemical Technology of Russia, Miusskaya Square 9, Moscow, Russia

Abstract

This paper presents basic information about applications, properties and extraction of titanium dioxide from liquid technogenic waste. Titanium dioxide is widely used in the production of ceramics, electrodes, etc. During the experiments using filtration, a recovery rate of 95% was achieved. Using the electroflotation method, a recovery rate of up to 50% was achieved. Subsequently, when complex additives are added, the degree of extraction by the electroflotation method reaches 95%.

Keywords: water treatment, titanium dioxide, electroflotation.

Corresponding Author:
A.V. Kolesnikov
artkoles@list.ru

Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

The purpose of this study is to determine the directions of increasing the efficiency of electroflotation extraction of TiO_2 from aqueous solutions of electrolytes in the presence of various additives (flocculants, surfactants, coagulants).

Titanium dioxide is widely used in the production of paints, enamels, paper, polymer compositions, functional ceramics, as well as in the preparation of insoluble anodic materials for electrochemical processes [1]. The requirements for titanium oxides are constantly increasing. Compositions of a suspension of an aqueous solution of titanium dioxide in the presence of surfactants are of most interest [2–5]. Due to the expansion of the use of titanium dioxide, especially small particles, when using sol-gel technologies in technological processes, liquid industrial waste containing colloidal-resistant TiO_2 compositions in aqueous electrolyte solutions is generated.

It is known that metal oxides and hydroxides, including TiO_2, are colloidal-stable systems in aqueous solutions, have a small particle size, are difficult to undergo sedimentation and filtration processes, and often become a source of environmental pollution [3, 6]. All non-ferrous heavy and rare earth metals and their compounds are toxic. The MAC for titanium oxide is 0.1...0.01 mg/L. The MAC values for other titanium compounds

are 0.1 mg/L. Various methods are used to extract fine particles of oxides and hydroxides, such as sedimentation, filtration, flotation, and electroflotation [6].

In this regard, the development of methods for the efficient extraction of the dispersed phase of TiO_2 is an urgent task. Traditional sedimentation, filtration and flotation methods for finely dispersed TiO_2 particles are ineffective. Publications on the electroflotation extraction of TiO_2 are sparse. Of interest is the work [7] on flotation extraction of TiO_2 using a collector reagent with a concentration of 100...300 mg/L per 1 g of TiO_2.

Studies conducted on the electroflotation of metal oxides and hydroxides [8, 9] showed that the process is most efficient for particles of a dispersed phase with sizes from 10 to 100 microns, having a small positive or zero charge (ζ-potential equal to 0...+5 mV). With strongly negatively charged particles the process is less efficient.

Laboratory studies of the efficiency of the electroflotation extraction of particles of the dispersed phase of titanium oxide from aqueous solutions were carried out in a non-flow electroflotator with an insoluble anode. The column of the electroflotator is made of glass, the cross-sectional area is 10 cm^2, the volume of the treated solution is 500 ml, the height of the apparatus is 800 mm, the sampling valve is located 40 mm above the electrode block. The electrode block includes an insoluble anode made of DSA (dimensionally stable anodes) (a titanium base with a film coating of cobalt and ruthenium oxides deposited by thermal decomposition of a mixture of their salts) and a cathode 5 made of stainless steel mesh with a mesh size of 0.5×0.4 mm, wire thickness 0.3 mm.

The efficiency of the electroflotation extraction of titanium TiO_2 from aqueous solutions was evaluated by the degree of extraction α, which is calculated as the ratio of the difference between the initial C_{in} and final C_{fin} particle content in the solution to the initial content:

$$\alpha = \frac{Cin - Cfin}{Cin} 100\ \%.$$

The initial and residual TiO_2 concentrations were measured by a HANNA HI 98703 portable turbidimeter in the range from 0.00 to 1000 NTU (nephelometric turbidity units). The particle size distribution was measured using the Analysette NanoTec / MikroTec / XT laser particle analyzer («Analysette 22 NanoTec»). Particle charge was measured using a modern laser submicron and nanoscale particle analyzer Malvern Zetasizer Nano, which also allows measuring the size of the nanoscale particles. Measurements are taken at the D. Mendeleev centre of collective usage.

Let us consider the experimental results on electroflotation (EF) and filtration (F) of TiO_2 present in aqueous solutions of electrolytes of various compositions. The effect of the pH of the solution on the efficiency of the EF extraction of TiO_2 in the range pH =

2... 12 in solutions of 1 g/L NaCl was studied. The experimental data are presented in table 1. It was found that the degree of extraction of the dispersed phase of TiO_2 by EF in the absence of surfactant does not exceed 10... 15% in the entire studied pH range. Filtration gives a degree of extraction of 80 – 90% (pH = 2 – 3) and 40 - 50% at pH = 4 – 11. Low effectiveness of electroflotation extraction is due to high colloidal stability of the system (precipitation occurs at 40... 50% in 4 hours) and small particle size.

The analysis showed that the particle size of TiO_2 does not exceed 1 μm. Electroflotation, as a rule, is used to remove particles of hydroxides, oxides, the size of which is 10... 100 microns. It is known that for TiO_2, H_30^+, $0H^-$ ions are potential-determining, determining the particle surface charge, the polarity and magnitude of the ζ-potential. The isoelectric point for TiO_2 is determined in the pH range = 6. In solutions at pH = 6–11, the ξ-potential magnitude is -5... -20 mV.

Table 1: The effect of the pH of the solution on the extraction of TiO_2 from aqueous solutions by electroflotation and filtration using anionic surfactants (NaDDS) and cationic surfactants (DDAC).

pH	α, %					
	without surfactants		NaDDS		DDAC	
	EF	F	EF	F	EF	F
2	12	84	11	89	12	87
3	16	90	37	84	26	79
4	12	52	11	67	16	75
5	8	43	10	75	14	71
6	4	41	20	70	12	64
7	4	41	20	73	14	66
8	4	42	22	70	5	43
9	4	43	29	71	6	44
10	8	45	14	71	5	42
11	6	48	18	77	6	47

Experimental conditions: C_{in} TiO_2 – 50 mg/L, C_{in} NaCl – 1 g/L; C_{in} surfactants – 5 mg/L (anionic – 5 mg/L; cationic surfactant – 5 mg/L; I = 0,4 A/L; τ = 20 min; F – filtration; EF – electroflotation.

The analysis shows that when filtering on a fine “blue ribbon” filter, it is possible to filter out particles larger than 1 μm. The filter does not trap particles the size of 0.1... 0.5 μm, and TiO_2 particles pass into solution. It is noted that with an increase in pH = 4... 12, approximately 50% of the particles have a size of 1 μm. With the addition of the anionic NaDDS surfactants, the degree of TiO_2 extraction increases to 20... 40%. The maximum degree of extraction is observed at pH = 3. This effect is due to the enlargement of the dispersed phase. The presence of surfactants in the system leads to an increase in the

efficiency of filtration processes from 40... 50 to 70... 75%. As studies have shown, in anionic surfactants, the adsorption region is pH = 2... 6.

The presence of the cationic surfactant DDAC has practically no effect, the degree of extraction increases by 5%. The absence of the effect of the cationic surfactants is associated with the difficulty of their adsorption on particles carrying a positive charge (pH = 2... 6) and a small negative charge (pH = 6... 10).

It was established that flocculants of different nature Zetag 8185 (K), Praestol 2530 (A) do not have a positive effect at pH = 2... 11, the degree of extraction does not exceed 15%. It was noted that the addition of amphoteric surfactants (beta-surfactant AP.45 and beta-surfactant A.1214.30) to the solution leads to an increase in the degree of extraction (up to 35 and 26%, respectively). In solutions containing 1 g/L Na_2SO_4, pH = 3.5, with the addition of a nonionic surfactant (PEG -1500), the degree of TiO_2 extraction is 45... 50%. During filtration, it is possible to extract 95% TiO_2 due to particle enlargement. The addition of a coagulant (Aqua-Aurat 10 and Aqua-Aurat 30) containing Al^{3+} ions does not increase the degree of TiO_2 extraction.

The influence of coagulants (Fe, Al), as well as powdered coal (Ou-B) on the efficiency of the electroflotation process was investigated. The introduction of these additives leads to an improvement in the dispersed phase of TiO_2 – $Me(OH)_3$ (pH = 6.0), TiO_2 – $Me(OH)_2$ (pH = 10.0), TiO_2 – Ou-B (pH = 3.0) and significantly increases the efficiency of the electroflotation process. Some experimental data are shown in table 2.

Table 2: The effect of the pH of the solution, the nature of the electrolyte and the additive (coagulant) on the degree of electroflotation extraction of TiO_2.

pH	additive	α, %			
		Na_2SO_4		NaCl	
		without	with	without	with
3.0	coal	16	56	12	70
6.0	Al^{3+}	6	64	8	54
	Fe^{3+}	6	60	8	95
10.0	Cu^{2+}	18	87	45	92
	Zn^{2+}	18	92	45	90

Experimental conditions: I=0,4 A/L, C(NaCl)= 1 g/L, C(Na_2SO_4)= 1 g/L, C(TiO_2)= 50 mg/L, C(additive: Me^{2+},Me^{3+}, coal)= 5 mg/L, τ=20 min.

It is noted that the degree of extraction increases to 90-95%. The process is most efficient in NaCl, the degree of extraction reaches maximum values in 10-15 minutes.

Studies have shown that electroflotation extraction of TiO_2 without additives, flocculants, surfactants, coagulants is inefficient (α = 20-30%). That is primarily associated with particle size (<1 μm). During the formation of the TiO_2 flotation complex - Me

hydroxide, the efficiency of the process increases, the degree of extraction reaches 90-95%. The conditions for achieving the degree of TiO_2 extraction up to 99% are determined. Technological solutions are in patenting stage.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No. 18-29-24010

References

[1] Kolesnikov, V. A., *et al*. (2016). Metal Oxides – Promising Materials for Electrochemical Processes. *Glass and cermics*, issue 12, pp. 23 – 28.

[2] Hosokawa, M., *et al*. (2007). *Nanoparticle Technology Handbook*. Amsterdam: Elsevier, pp. 644.

[3] Golikova, E. V., Chernoberezhsky, Y. M. and Johanson, O. M. (2000). On the Correlation of Aggregative Stability and Integrated Electro-Surface Characteristics of Oxide Dispersions. *Colloid Journal*, vol. 62, pp. 596 – 605.

[4] Pavlova-Verevkina, O. B., *et al*. (2009). The Effect of Electrolytes on the Slow Aggregation of Nanocrystals TiO_2. *Colloid Journal*, vol. 71, issue 4, pp. 522.

[5] Xu, G., *et al*. (2003). Effect of Complexation on the Zeta Potential of Titanium Dioxide Dispersions. *J. Dispersion Sci. Technol*., vol. 24, p. 527.

[6] Kolesnikov, V. A., Menshutina, N. V. and Desyatov, A. V. (2016). *Equipment, Technologies and Design of Wastewater Treatment Systems*. Moscow. Deli Plus, p. 288.

[7] Shen, Y. (1998). Colloidal Titanium Dioxide Separation from Water by Foam Flotation. *Separation Science and Technology*, vol. 54, issue 16, pp. 2623 – 2635.

[8] Kolesnikov, V. A., *et al*. (2017). Electroflotation Extraction of Sparingly Soluble Compounds of Non-Ferrous and Rare-Earth Metals from Liquid Technological Waste. *Pure and Applied Chemistry*, vol. 89, issue 10, pp. 1535 – 1541.

[9] Kolesnikov, V. A., *et al*. (2017). Electroflotation in the Processes of Water Purification and Extraction of Valuable Components from Liquid Industrial Wastes: A Review. *Theoretical foundations of chemical technology*, vol. 51, issue 4, pp. 361 – 375.